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European Patent Office
Office européen des brevets



(11) Publication number:

0 422 683 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 90119631.1

(22) Date of filing: 12.10.90

(51) Int. Cl.⁵: **D06P 5/08, D06P 5/06,
D06P 1/607, D06P 1/52,
D06P 1/48, D06P 1/62,
D06P 1/667**

(30) Priority: 13.10.89 JP 265011/89

(43) Date of publication of application:
17.04.91 Bulletin 91/16

(64) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

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(54) Washing-off agent composition for dyed cellulose fiber articles.

(57) Washing-off agent composition for dyed cellulose fiber articles comprising an effective amount of a polyoxyalkylene derivative of organic amine (poly (1 to 5) alkylene (C2 to C6) polyamine alkyleneoxide adducts which may contain alkyl (or alkenyl) groups, aromatic amine alkyleneoxide adducts or nitrogen-containing derivatives of high polymer) as an essential ingredient reduces or shortens the washing-off steps for reactive dyes with improved fastness of color for any kind of reactive dyes. Presence of a water-soluble high polymer having a carboxylic group and/or an anionic surfactant promotes removal of unfixed and hydrolyzed dyes from dyed articles to improve fastness of color.

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WASHING-OFF AGENT COMPOSITION FOR DYED CELLULOSE FIBER ARTICLES

FIELD OF THE INVENTION

This invention relates to a washing-off agent composition for washing-off cellulose fibers dyed or printed mainly by reactive dyes or dyed articles inclusive of these dyed or printed cellulose fibers.

BACKGROUND

The following proposals, for example, have been made in connection with washing-off agents for use in post-soaping of dyed cellulose fiber articles.

(a) The JP-Patent-Kokai Publication No.56-(1981)-63081 discloses "a soaping agent for cellulose fibers composed of carboxyl group containing water-soluble high polymers or high polymer materials and having a molecular weight of not lower than 300 (synthetic water-soluble high polymers such as polyacrylic acids) part or all of which may be in the form of salts".

(b) The JP-Patent-Kokai Publication No.58-(1983)-41981 discloses "a soaping agent for cellulose fiber printed articles comprising an aqueous solution of a maleic anhydride-isoamylene and/or amylene copolymer at a molar ratio of 3/7 to 7/3 with a molecular weight of not less than 300, part or all of which may be in the form of salts".

(c) The JP-Patent-Kokoku Publication No.59-(1984)-29718 teaches "the use for soaping of an aqueous solution of a polymer containing carboxylic groups, at least part of which is neutralized in the form of salts".

(d) The JP-Patent-Kokai Publication No.61-(1986)-215769 discloses

i) a water-soluble or water-dispersible polymer comprising, as an essential ingredient, at least one monomer selected from the group consisting of unsaturated carboxylic acids and derivatives thereof, and

ii) "a soaping agent for dyed cellulose fiber goods or articles containing a formalin condensate or salt thereof of sulfonation products of polycyclic aromatic compounds, as an essential ingredient, said soaping agent occasionally containing hydrocarbon residues as substituents".

(e) The JP-Patent-Kokai Publication No.61-(1986)-239090 discloses a soaping agent for dyed cellulose fiber articles containing, as an essential ingredient, a vinyl polymer having a pyrrolidone skeleton".

(f) The JP-Patent-Kokai Publication No.63(1988)-

135581 discloses a soaping agent for dyed cellulose fiber articles containing organic phosphonic acids and/or salts thereof as effective ingredients".

(g) The JP-Patent-Kokai Publication No.63-(1988)-175184 discloses a soaping agent for reactive dyeing with a weight mean molecular weight of 2,000 to 1,500,000 containing polystyrene sulfonic acids and/or salts thereof".

(h) The JP-Patent-Kokai No.57(1982)-61783 teaches "a soaping operation comprising the sequential steps of

i) soaping by a first bath containing metal ions and an anionic or nonionic surfactant,

ii) soaping by a second bath containing peroxide and an anionic or nonionic surfactant, and

iii) treatment by a third bath containing a chelating agent".

SUMMARY OF THE DISCLOSURE

Problems to be solved by the invention

In the field of dyeing or printing, in keeping up with the demand for energy saving, shortening and reduction of steps and reduction in waste water load, there exists presently a strong need for a washing-off agent with a high added value whereby the shortening and reduction of steps, simplification of operation, superior dyeing quality and fasteners of color may be achieved. Above all, in the field of dyeing with reactive dyes, it is rather difficult to remove unfixed dyes and hydrolyzed dyes from dyed articles by a washing-off treatment and hence a high degree of fasteners of color cannot be realized. Although the above mentioned various technologies have been disclosed to overcome these difficulties, these technologies are not fully satisfactory to meet the above demand.

In addition, the conventional soaping agent exhibits soaping properties and fastness of color only for certain specified reactive dyes, without being effective for reactive dyes in their entirety. Hence, it becomes occasionally necessary to use various washing-off agents for various types of the reactive dyes and, in order to avoid this, it becomes necessary to restrict the range of the reactive dyes which may be employed for dyeing.

On the other hand, the washing-off treatment described in the JP-Patent-Kokai Publication No.57(1982)-61783 is disadvantageous in that it involves a number of operating steps, while being

low in operability and efficiency.

Objects of the Invention

It is therefore an object of the present invention to provide a washing-off agent composition for dyed cellulose fiber articles which is free from the above mentioned deficiencies of the prior art.

Further object of the present invention will become clear in the entire disclosure.

For accomplishing the above object, the present invention provides following three types of composition:

- (i) a washing-off agent composition for dyed cellulose fiber articles comprising, as an essential ingredient, an effective amount of a polyoxyalkylene derivative of an organic amine;
- (ii) a washing-off agent composition for dyed cellulose fiber articles comprising, as essential ingredients, an effective amount of a polyoxyalkylene derivative of an organic amine, and a water-soluble high polymer having a carboxylic group or an anionic surfactant; and
- (iii) a washing-off agent composition for dyed cellulose fiber articles comprising, as essential ingredients, an effective amount of a polyoxyalkylene derivative of an organic amine, a water-soluble high polymer having a carboxylic group, and an anionic surfactant.

Preferably, the polyoxyalkylene derivative of an organic amine is one or more of poly (1 to 5) alkylene (C2 to C6) polyamine alkyleneoxide adducts which may contain alkyl (or alkenyl) groups, aromatic amine alkyleneoxide adducts or nitrogen-containing derivatives of high polymer. Preferably, the amount of added alkylene oxides is 1 to about 200 (more preferably, 1 to 100, or further 1 to 50).

The washing-off agent composition (i) of the present invention, comprising an effective amount of the polyoxyalkylene derivative of the organic amine, is capable of effectively removing unfixed dyes and hydrolyzed dyes from the dyed articles.

The washing-off agent composition (ii) of the present invention, comprising an effective amount of a polyoxyalkylene derivative of an organic amine, a water-soluble high polymer having a carboxylic group or an anionic surfactant, is capable of effectively removing unfixed dyes or the like from the dyed articles irrespective of the types of the reactive dyes and improving the rate of removal of the unfixed dyes etc. from the dyed articles.

The washing-off agent composition (iii) of the present invention, comprising an effective amount of a polyoxyalkylene derivative of an organic amine, a water-soluble high polymer having a carboxylic group and an anionic surfactant is capable of more effectively removing unfixed or hydrolyzed dyes from

the dyed articles, irrespective of the types of the reactive dyes, by virtue of the synergistic effects of the three components, thereby achieving a high degree of fastness of color.

It is also possible with the washing-off agent composition containing the above mentioned two or more of the above specified components as essential ingredients, to shorten or reduce the soaping steps following the dyeing regardless of the types of the reactive dyes. These effects become most pronounced with the washing-off agent composition containing all of the above mentioned three specified components. As the polyoxyalkylene derivatives of organic amine those of alkylene diamine or alkanol amine may be used.

PREFERRED EMBODIMENTS

On account of the content of the polyoxyalkylene derivative of the organic amine as the essential ingredient of the washing-off agent composition for dyed cellulose fiber articles, unfixed and hydrolyzed dyes may be effectively removed from the dyed articles in the course of the washing-off treatment. In addition, if the water-soluble high polymer containing carboxylic group or the anionic surfactants capable of further improving the washing-off properties are contained as the second component in the polyoxyalkylene derivative of the organic amine, it becomes possible to improve the rate of removal of the unfixed dyes and the hydrolyzed dyes from the dyed articles.

If the anionic surfactant is contained in the washing-off agent composition of the present invention, in addition to the effective amount of the polyoxyalkylene derivative of the organic amine and the water-soluble high polymer containing carboxylic groups, it becomes possible, by virtue of the synergistic effect of these three components, to remove unfixed dyes and hydrolyzed dyes from dyed articles to achieve a higher degree of fastness of color for any type of the reactive dyes without limitation to specific types of the reactive dyes.

With the washing-off agent composition of the present invention, preferably 0.01 to 20 parts by weight (more preferably 0.05 to 10 parts by weight) of the water-soluble high polymer containing a carboxylic group or further 0.01 to 10 parts by weight (more preferably 0.05 to 5 parts by weight) of the anionic surfactant are contained to 1 parts by weight of the polyoxyalkylene derivative of the organic amine.

The washing-off agent composition of the present invention may contain suitable solvents, such as water, in addition to the above mentioned three specified components. It is preferred that at

least 3 wt.% of the polyoxyalkylene derivative of the organic amine is contained in the washing-off agent composition and that at least 0.09 wt.% of the water-soluble high polymer is contained in the composition if the water-soluble high polymer containing the carboxylic group, or at least 0.05 wt.% of the anionic surfactant if the anionic surfactant are contained in the composition, respectively. If the above mentioned three components are present in the above mentioned respective ranges, these components may function more effectively.

Among polyoxyalkylene derivatives of the organic amine, there are aliphatic amine alkylene oxide adducts, aromatic amine alkylene oxide adducts and nitrogen-containing derivatives of high polymer.

The aliphatic amine alkylene oxide adducts include polyoxyalkylene (C2 to C4) alkyl- (or alkenyl- or 2-hydroxyalkyl-) amines, n-polyoxyalkylene n,n-dialkyl- (or alkenyl-) amines, poly (1 to 5) alkylene (C2 to C6) polyamine (preferably containing 10 or less amine groups) alkylene oxide adducts which may contain alkyl (or alkenyl or 2-hydroxyalkyl) groups, alkyl biguanidine alkylene oxide adducts and aminoethyl (or alkylaminoethyl) piperazine alkylene oxide adducts, or the like.

The aromatic amine alkylene oxide adducts include n,n-dipolyoxyethylene, benzylamines (or phenylamines or naphthylamines), and phenylene diamine (or methylphenylene diamine, or xylylene diamine) alkylene oxide adducts, or the like.

The nitrogen-containing derivatives of high polymer include formalin condensates of polyoxyethylene alkyl (or alkenyl) (C1 to C12) phenol (or generally phenol including phenol derivatives) and N-polyoxyethylene polyalkylene (C2 to C6) polyamine (or N-polyoxyethylene alkyl (or alkenyl) (C8 to C24) amine), or the like.

The washing-off agent compositions of the present invention may include one or more of polyoxyalkylene derivatives of the above mentioned organic amines.

The water-soluble high polymers containing carboxylic groups include natural water-soluble high polymers, semi-synthetic water-soluble high polymers obtained by chemical synthesis of natural water-soluble or -insoluble high polymers, and synthetic water-soluble high polymers obtained by chemical synthesis of other polymeric materials.

Among the natural water-soluble high polymers, there are gum arabic, pectinic acid, Karaya gum, alginic acid, xanthane rubber and hyaluronic acid etc.

Among the semi-synthetic water-soluble high polymers, there are graft polymers and carboxymethylates of natural high polymers. Examples of graft polymers of natural high polymers include graft polymers of cellulose or starch and unsatu-

rated carboxylic acids, such as acrylic acid, or derivatives thereof. Examples of carboxymethylates of natural high polymers include carboxymethylates of cellulose or starch.

Among the synthetic water-soluble high polymers, there are, for example, homopolymers derived from unsaturated organic acids, such as acrylic acid, methacrylic acid or maleic acid, copolymers of these unsaturated organic acids with ethylenic unsaturated monomers, and salts thereof. Those synthetic water-soluble high polymers include polymers of acrylic acid, polymers of methacrylic acid, acrylic acid-methacrylic acid copolymer, acrylic acid-vinyl acetate copolymer, acrylic acid-maleic acid copolymer, acrylic acid-ethylene copolymer, maleic acid-isobutylene copolymer, maleic acid-styrene copolymer, alkali metal salts and organic amine salts thereof.

The viscosity of the water-soluble high polymers (at a concentration of 2 per cent) is preferably 10^{-2} to 100 Pa s (=10 to 100,000 cP) and more preferably 10^{-2} to 10 Pa s (=10 to 10,000 cP).

The washing-off agent compositions of the present invention may include, for example, one or more of the above mentioned water-soluble high polymers.

The anionic surfactants may include, for example, sulfonic acids, esters of sulfonic acid, esters of phosphoric acid, carboxylic acid, or salts thereof; polycondensate type high-polymer anionic surfactants or salts thereof; and formalin condensates of aromatic sulfonation products.

The sulfonic acids and salts thereof may include, for example, dialkylsulfosuccinic acid, n-alkylsulfosuccinic acid mono- or diamides, n-methyl-n-alkyltaurine, alkane (or α -olefin, hydroxyalkane) sulfonic acid, straight-chained (or branched) alkylbenzene sulfonic acid, alkyl naphthalene sulfonic acid, polyoxyalkylene alkylphenol sulfonic acid and salts thereof or the like.

The esters of sulfuric acid and salts thereof may include, for example, sulfurated castor oil, aliphatic acid alkyl ester sulfuric acid esters, alkyl sulfuric acid esters, polyoxyalkylene ether sulfuric acid esters, aliphatic acid monoglyceride sulfuric acid esters, polyoxyalkylene alkylamide sulfuric acid esters, polyoxyalkylene alkyl phenyl ether sulfuric acid esters, and salts thereof.

The esters of phosphoric acid and salts thereof may include, for example, alkyl phosphoric acid esters, polyoxyalkylene alkylether phosphoric acid esters, polyoxyalkylene phenylether phosphoric acid esters and salts thereof.

The carboxylic acids and salts thereof may include, for example, n-acyloyl sarcosine (or alanine or amino acids), polyoxyalkylene alkylether carboxylic acids, polyoxyalkylene alkylphenylether carboxylic acids, α -carboxymethylalkanic (or al-

kenic) acids and salts thereof.

The polycondensate type high polymer anionic surfactants and salts thereof may include, for example, amino acid condensates, ligninsulfonic acid and collagen hydrolysates.

The washing-off agent compositions of the present invention may include, for example, one or more of the anionic surfactants.

The washing-off agent compositions of the present invention may be used for washing-off operations either directly or after dilution with water or the like solvents. When the compositions are used after dilution with water or the like solvent, they are diluted to a concentration at which the polyoxyalkylene derivative of the organic amine may exhibit its effect. For example, the polyoxyalkylene derivative of the organic amine is contained in a washing-off bath at a concentration preferably approximately of 0.1 to 10g/lit. (more preferably 0.5 to 4 g/lit.).

The washing-off conditions may include, for example, a bath temperature of 40 to 100°C and the washing-off time duration of 5 to 30 minutes. After the washing-off, the dyed products may be washed with cold, warm or hot water upon necessity.

The present invention is further disclosed in more detail referring to the preferred embodiments as the following Examples.

EXAMPLES

Example 1

20 parts by weight of oleylamine (EO)₁₅ were diluted in 80 parts by weight of water to give a composition of the present invention.

Example 2

20 parts by weight of ethylenediamine (PO)₁₀-(EO)₁₅ were diluted in 80 parts of water to give a composition of the present invention.

Examples 3 to 6

10 parts by weight of oleylamine (EO)₁₅ or ethylene diamine (PO)₁₀(EO)₁₅ and 5 parts by weight of carboxymethylcellulose referred to hereinafter as CMC (2%, 5×10^{-2} Pa s = 50cP) or 5 parts by weight of gum arabic, were mixed together and diluted with 85 parts by weight of water to give four different types of the compositions of the present invention.

Examples 7 to 10

10 parts by weight of oleylamine (EO)₁₅ or ethylene diamine (PO)₁₀(EO)₁₅ and 10 parts by weight of sodium dodecylsulfonate or tridecyl (EO)₃ sodium acetate were mixed together and diluted with 80 parts of water to give four different types of the compositions of the present invention.

Example 11

10 parts by weight of oleylamine (EO)₁₅, 5 parts by weight of CMC(2%, 5×10^{-2} Pa s = 50 cP) and 10 parts by weight of sodium dodecylsulfonate were mixed together and diluted with 75 parts by weight of water to give a washing-off agent composition of the present invention.

Example 12

15 parts by weight of ethylenediamine (PO)₁₀-(EO)₁₅, 3 parts by weight of sodium alginate (molecular weight, 50,000) and 10 parts by weight of sodium POE(3) tridecyl ether acetate were mixed together and diluted with 72 parts by weight of water to give a washing-off agent composition of the present invention.

Comparative Example 1

An organic phosphonic acid soaping agent described in JP-Patent-Kokai No.63(1988)-135581, i.e., sodium nitrilotris (methylene) triphosphonate-5 Na salt.

Comparative Example 2

A polyvinylpyrrolidone soaping agent described in JP-Patent-Kokai No.61(1986)-239090, having a molecular weight of 10,000.

Comparative Example 3

A polycarboxylic acid soaping agent described in JP-Patent-Kokoku Publication NO. 59(1984)-29718, which is sodium salt of polyacrylic acid having a molecular weight of 10,000.

Comparative Example 4

A soaping agent containing a sodium salt of maleic anhydride-isoamylene copolymer etc. as

described in JP-Patent-Kokai Publication No.58-(1984)-41981, in a molar ratio of 50/50 and having a molecular weight of 20,000.

Comparative Example 5

A soaping agent mainly composed of a carboxylic group containing water-soluble high polymer as described in JP-Patent-Kokai Publication NO.56-(1981)-63081, which is sodium salt of polymaleic acid having a molecular weight of 6,000.

Comparative Example 6

A polystyrene sulfonic acid soaping agent as described in JP-Patent Kokai Publication NO.63-(1988)-175184, which is sodium salt thereof and has a molecular weight of 10,000.

Comparative Examples 7 to 10

10 parts by weight of sodium dodecylsulfonate or sodium POE(3) tridecyl ether acetate and 5 parts by weight of CMC (2%, 5×10^{-2} Pa*s) or sodium alginate (molecular weight, 50,000) were mixed together and diluted with 85 parts of water to give four different compositions.

Soaping Tests

Washing-off operations were performed using the washing-off agent compositions of Examples 1 to 12 of the present invention and the soaping agents of the comparative Examples 1 to 10.

(1) Dyeing Method

A cotton knit cloth (non-mercerized) was dyed under conditions of 5.0 % owf (on weight fabric) each of the reactive dyes, 60 g/lit of Glauber's salt, 15 g/lit of soda ash, bath ratio of 1:15 and the dyeing time duration of 50 minutes. The reactive dyes employed are shown in Tables 1 and 2.

The dyes employed include following commercial dyes:

Red 195 Sumifix Supra B Red 3BF
Red 183 Cibacron Scarlet F-3G
Red 158 Levafix Red E-4BA
Red 120 Procion Red H-E3B
Red 21 Procion B.Red BB
Blue 79 Drimarene Navy X-RBL
Blue 21 Levafix Turq Blue E-G
Blue 4 Mikacion Blue RS

(2) Washing-off Method

For washing-off the dyed products obtained by the above dyeing method, 1.0 g/lit of the soaping agent of the compositions of the Examples or the soaping agents of the Comparative Examples in terms of pure (i.e., 100 per cent) components at the bath ratio of 1:25. Soaping was carried out at 95 °C for 20 minutes (for the inventive Examples), or the same soaping step was repeated (for the Comparative Examples). Then washing by hot water was carried out at 90 °C for 10 minutes. Finally, washing by water was carried out for 10 minutes. The washing articles were centrifuged and dried spontaneously. The dried articles were put to tests for determining fastness of color in order to determine to what extent unfixed dyes or hydrolyzed dyes remained on the dyed articles.

(3) Tests on Fastness of Color

Water fastness, washing fastness and rubbing fastness were tested in accordance with the methods prescribed in JIS L 0846A, JIS L 0844 A-2 and JIS L 0849 methods.

Evaluation was made by the contamination gray scale as prescribed in JIS L 0805.

Results

The results of evaluation of fastness of color following the washing-off are shown in Tables 1 and 2. It is seen from these Tables that the washing-off agent compositions of the present invention exhibit the fastness of color which is higher than that of the soaping agent of the Comparative Examples.

It is also seen that the washing-off agent compositions of the present invention (Examples 3 to 12) exhibit satisfactory washing-off properties for any reactive dyes. Above all, these washing-off agent compositions containing the above mentioned three components (Examples 11 and 12) exhibit extremely satisfactory washing-off properties for any reactive dyes.

On the other hand, when the soaping agents of the Comparative Examples are used, the washing-off properties for reactive dyes in general are insufficient and resoaping may occasionally become necessary. Conversely, the washing-off agent compositions of the present invention (Examples 3 to 12) exhibit satisfactory washing-off properties for any reactive dyes in general, so that the number of washing-off steps following the dyeing step may be reduced or shortened for any reactive dyes. This effect becomes most outstanding when the

washing-off agent compositions contain the above mentioned three specific components (Example 11 and 12).

It should be noted that the present invention is not limited to the specific embodiments or examples disclosed herein, and that modifications may be done without departing from the gist and concept of the present invention as defined in the appended claims.

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TABLE 1-1 (Soaping \times 1 time)

Friction Fastness, Water Fastness and Washing Fastness

Examples	Red 195				Red 183				Blue 21				Red 120			
	Rubbing		Water		Washing		Rubbing		Water		Washing		Rubbing		Water	
	Dry	Wet					Dry	Wet					Dry	Wet		
Ex. 1~2	B	C	B	B	B	B	B	C	B	C	C	C	C	x	C	C
Ex. 3~6	B	C	A	B	A	A	A	C	A	C	A	C	B	C	B	B
Ex. 7~10	B	C	B	B	B	B	B	C	B	C	B	B	B	C	B	C
Ex. 11~12	B	C	A	A	A	A	A	C	A	B	A	A	A	C	A	A

1st grade to less than 3rd grade x
 3rd grade to less than 4th grade C
 4th grade to less than 5th grade B
 5th grade A

TABLE 1-2 (Soaping x 1 time)

Friction Fastness, Water Fastness and Washing Fastness

Examples	Red 21				Red 158				Blue 4				Blue 79			
	Rubbing		Water		Washing		Rubbing		Water		Washing		Rubbing		Water	
	Dry	Wet					Dry	Wet					Dry	Wet		
Ex. 1~2	B	C	B	B	B	C	B	C	B	B	C	C	C	X	C	C
Ex. 3~6	A	C	B	A	A	C	B	C	A	A	B	B	B	C	B	B
Ex. 7~10	B	C	B	B	B	C	B	C	B	B	B	B	B	C	B	B
Ex. 11~12	A	B	A	A	A	C	A	C	A	A	B	B	A	B	B	A

1st grade to less than 3rd grade X
 3rd grade to less than 4th grade C
 4th grade to less than 5th grade B
 5th grade A

TABLE 2-1 (Soaping x 1 time)

Friction Fastness, Water Fastness and Washing Fastness

Comparative Examples	Red 195				Red 183				Blue 21				Red 120			
	Rubbing		Water		Rubbing		Water		Rubbing		Water		Rubbing		Water	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
C 1	B	C	B	B	C	X	C	C	C	X	C	C	C	X	C	C
C 2	C	X	C	B	C	X	C	C	C	X	C	B	C	X	B	B
C 3	C	X	C	C	B	C	C	C	B	C	C	C	B	C	B	B
C 4	C	X	C	C	B	C	C	C	B	C	C	C	B	C	B	B
C 5	C	X	C	C	B	C	C	C	B	C	C	C	B	C	B	B
C 6	B	C	B	B	C	X	C	C	C	X	C	C	C	X	C	B
C 7-10	B	C	B	C	B	C	C	C	C	X	C	C	C	X	X	X

1st grade to less than 3rd grade X
 3rd grade to less than 4th grade C
 4th grade to less than 5th grade B
 5th grade A

TABLE 2-2 (Soaping x 1 time)

Friction Fastness. Water Fastness and Washing Fastness

Comparative Examples	Red 21				Red 158				Blue 4				Blue 79			
	Rubbing		Water		Washing		Rubbing		Water		Washing		Rubbing		Water	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
C 1	B	C	B	B	B	C	B	C	B	C	B	C	C	X	C	C
C 2	B	C	B	B	B	C	C	X	C	C	C	C	C	X	C	C
C 3	B	C	B	B	B	C	B	X	C	C	C	C	B	C	B	B
C 4	B	C	B	B	B	C	B	X	C	C	C	C	C	X	C	C
C 5	B	C	B	B	B	C	B	X	C	C	C	C	B	C	B	B
C 6	B	C	B	B	B	C	B	C	B	B	B	B	C	X	C	C
C 7~10	B	C	C	B	B	C	B	C	B	C	C	X	C	X	X	X

1st grade to less than 3rd grade X
 3rd grade to less than 4th grade C
 4th grade to less than 5th grade B
 5th grade A

Washing-off agent composition for dyed cellulose fiber articles comprising an effective amount of a polyoxyalkylene derivative of organic amine (poly (1 to 5) alkylene (C2 to C6) polyamine alkyleneoxide adducts which may contain alkyl (or alkenyl) groups, aromatic amine alkyleneoxide adducts or nitrogen-containing derivatives of high polymer) as an essential ingredient reduces or shortens the washing-off steps for reactive dyes with improved fastness of color for any kind of reactive dyes. Presence of a water-soluble high polymer having a carboxylic group and/or an anionic surfactant promotes removal of unfixed and hydrolyzed dyes from dyed articles to improve fastness of color.

Claims

1. A washing-off agent composition for dyed cellulose fiber articles comprising an effective amount of a polyoxyalkylene derivative of organic amine as an essential ingredient.
2. A washing-off agent composition for dyed cellulose fiber articles comprising an effective amount of a polyoxyalkylene derivative of organic amine and a water-soluble high polymer having a carboxylic group or an anionic surfactant.
3. A washing-off agent composition for dyed cellulose fiber articles comprising effective amount of a polyoxyalkylene derivative of organic amine, a water-soluble high polymer having a carboxylic group and an anionic surfactant.
4. The washing-off agent composition as defined in any one of claims 1 to 3, characterized in that the polyoxyalkylene derivative of organic amine is one or more of poly (1 to 5) alkylene (C2 to C6) polyamine alkyleneoxide adducts which may contain alkyl (or alkenyl) groups, aromatic amine alkyleneoxide adducts or nitrogen-containing derivatives of high polymer.
5. The washing-off agent composition as defined in claim 4, characterized in that the polyoxyalkylene derivative of organic amine has added alkylene oxide in an amount of 1 to 200 (preferably 1 to 100, more preferably 1 to 50).
6. The washing-off agent composition as defined in any one of claims 2 to 5 characterized in that the water-soluble high polymer is a natural water-soluble high polymer having a carboxylic group.
7. The washing-off agent composition as defined in any one of claims 2-6, characterized in that the water-soluble high polymer is present in an amount of 0.01 to 20 (preferably 0.05 to 10) parts by weight relative to one parts by weight of the polyoxyalkylene derivative of organic amine.
8. The washing-off agent composition as defined in any one of claims 2-6, characterized in that the anionic surfactant is present in an amount of 0.01 to 10 (preferably 0.05 to 5) parts by weight relative to the polyoxyalkylene derivative of organic amine.
9. The washing-off agent composition as defined in any one of claims 1-8, characterized in that an aqueous solvent is further present and the polyoxyalkylene derivative of organic amine is present in an amount of at least 3 wt percent.
10. The washing-off agent composition as defined in any one of claims 2-8, characterized in that an aqueous solvent is further present and the water-soluble high polymer is present in an amount of at least 0.09 wt percent.
11. The washing-off agent composition as defined in any one of claims 2-8, characterized in that an aqueous solvent is present and the anionic surfactant is present in an amount of at least 0.05 wt percent.
12. The washing-off agent composition as defined in any one of claims 1-11, characterized in that the polyoxyalkylene derivative of organic amine is selected from aliphatic amine alkylene oxide adducts, aromatic amine alkylene oxide adducts and nitrogen-containing derivatives of high polymer.
13. The washing-off agent composition as defined in claim 12, characterized in that the aliphatic amine alkylene oxide adduct is selected from polyoxyalkylene (C2 to C4) alkyl- (or alkenyl- or 2-hydroxyalkyl-) amines, n-polyoxyalkylene n,n-dialkyl-(or alkenyl-)amines, poly (1 to 5) alkylene (C2 to C6) polyamine (preferably containing 10 or less amine groups) alkylene oxide adducts which may contain alkyl (or alkenyl or 2-hydroxyalkyl) groups, alkyl biguanidine alkylene oxide adducts and aminoethyl (or alkylaminoethyl) piperazine alkylene oxide adducts.
14. The washing-off agent composition as defined in claim 12, characterized in that the aromatic amine alkylene oxide adduct is selected from n,n-dipolyoxyethylene, benzylamines (or phenylamines or naphthylamines), and phenylene diamine (or methylphenylene diamine, or xylylene diamine) alkylene oxide adducts.
15. The washing-off agent composition as defined in claim 12, characterized in that the nitrogen-containing derivative of high polymer is selected from formalin condensates of polyoxyethylene alkyl (or alkenyl) (C1 to C12) phenol (or generally phenol including phenol derivatives) and N-polyoxyethylene polyalkylene (C2 to C6) polyamine (or N-polyoxyethylene alkyl (or alkenyl) (C8 to C24) amine).
16. The washing-off agent composition as defined in any one of claims 2-5 and 7-15, characterized in that the water-soluble high polymer is selected from natural water-soluble high polymers, semi-

synthetic water-soluble high polymers obtained by chemical synthesis of natural water-soluble or -insoluble high polymers, and synthetic water-soluble high polymers obtained by chemical synthesis of other polymeric materials.

17. The washing-off agent composition as defined in claim 6 or 16, characterized in that the natural water-soluble high polymer is selected from gum arabic, pectinic acid, Karaya gum, alginic acid, xanthane rubber and hyaluronic acid.

18. The washing-off agent composition as defined in claim 16 characterized in that the semi-synthetic water-soluble high polymer is selected from graft polymers (preferably, graft polymers of cellulose or starch and unsaturated carboxylic acids, such as acrylic acid, or derivatives thereof) and carboxymethylates of natural high polymers (preferably, carboxymethylates of cellulose or starch).

19. The washing-off agent composition as defined in claim 16 characterized in that which the synthetic water-soluble high polymer is selected from homopolymers derived from unsaturated organic acids, such as acrylic acid, methacrylic acid or maleic acid, copolymers of these unsaturated organic acids with ethylenic unsaturated monomers, and salts thereof (preferably, polymers of acrylic acid, polymers of methacrylic acid, acrylic acid-methacrylic acid copolymer, acrylic acid-vinyl acetate copolymer, acrylic acid-maleic acid copolymer, acrylic acid-ethylene copolymer, maleic acid-isobutylene copolymer, maleic acid-styrene copolymer, alkalimetal salts and organic amine salts thereof).

20. The washing-off agent composition as defined in any one of claims 2-19, characterized in that the viscosity of the water-soluble high polymers (at a concentration of 2 percent) is 10^{-2} to $100 \text{ Pa}\cdot\text{s}$ (preferably, 10^{-2} to $10 \text{ Pa}\cdot\text{s}$).

21. The washing-off agent composition as defined in any one of claims 2-20, characterized in that the anionic surfactant is selected from sulfonic acids, esters of sulfonic acid, esters of phosphoric acid, carboxylic acid, or salts thereof; polycondensate type high-polymer anionic surfactants or salts thereof; and formalin condensates of aromatic sulfonation products.

22. The washing-off agent composition as defined in claim 21, characterized in that the sulfonic acids and salts thereof are selected from dialkylsulfosuccinic salts, n-alkylsulfosuccinic acid mono- or diamides, n-methyl-nalkyltaurine, alkane (or α -olefin, hydroxyalkane) sulfonic acid, straight-chained (or branched) alkylbenzene sulfonic acid, alkyl-naphthalene sulfonic acid and polyoxyalkylene alkyl-phenol sulfonic acid, and salts thereof.

23. The washing-off agent composition as defined in claim 21, characterized in that the esters of sulfuric acid and salts thereof are selected from

sulfurated castor oil, aliphatic acid alkyl ester sulfuric acid esters, alkyl sulfuric acid esters, polyoxyalkylene ether sulfuric acid esters, aliphatic acid monoglyceride sulfuric acid esters, polyoxyalkylene alkylamide sulfuric acid esters, polyoxyalkylene alkyl phenyl ether sulfuric acid esters, and salts thereof.

24. The washing-off agent composition as defined in claim 21, characterized in that the ester of phosphoric acid and salts thereof is selected from alkyl phosphoric acid esters, polyoxyalkylene alkylether phosphoric acid esters, polyoxyalkylene phenylether phosphoric acid esters and salts thereof.

25. The washing-off agent composition as defined in claim 21, characterized in that the carboxylic acids and salts thereof are selected from n-acyloyl sarcosine (or alanine or amino acids), polyoxyalkylene alkylether carboxylic acids, polyoxyalkylene alkylphenylether carboxylic acids, α -carboxymethylalkanic (or alkenic) acids and salts thereof.

26. The washing-off agent composition as defined in claim 21, characterized in that the polycondensate type high polymer anionic surfactants and salts thereof are selected from amino acid condensates, ligninsulfonic acid and collagen hydrolysates.

27. The use of the washing-off agent composition as defined in any one of claims 1-26, characterized in that the polyoxyalkylene derivative of organic amine is present in a washing-off agent bath at a concentration of 0.1 to 10 g/lit. (preferably 0.5 to 4 g/lit.).



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EUROPEAN SEARCH REPORT

Application Number

EP 90 11 9631

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
A	DE-A-2843645 (BASF AG) * the whole document *	1-5, 12-14, 27	D06P5/08 D06P5/06 D06P1/607 D06P1/52 D06P1/48 D06P1/62 D06P1/667
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22 JANUARY 1991	Examiner DELZANT J-F.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published no, or after the filing date D : document cited in the application I : document cited for other reasons & : member of the same patent family, corresponding document			